Method 310 - Appendix A

PROPELLANT COLLECTION PROCEDURES

1 APPLICATION

The procedure applies to modify ASTM D 3074-94 and D 3063-94 to allow collection of the propellant for analysis and density measurement for metal aerosol containers and glass aerosol containers, respectively. These modified procedures also retain the aerosol standard terminology listed in ASTM D 3064-~~89~~ *97*. ~~The aerosol product container is pierced and the propellant is bled into an evacuated manifold. After the manifold reaches atmospheric pressure, approximately 1 liter of the propellant is collected in a clean, evacuated Tedlar bag. For density measurement the propellant is collected into an evacuated 250 mL glass dilution bulb that has been weighed to the nearest 0.1 mg. After filling, the dilution bulb is re-weighed to determine the density of the propellant. Alternately, density may be determined using a Density/Specific Gravity Meter. The Tedlar bag with the propellant aliquot is taken to the laboratory for analysis.~~

2 LIMITATIONS

Nitrogen analysis: Nitrogen may be used as a component of the propellant system. Ambient air is 78 percent nitrogen and may be present as a contaminate in the system prior to sample collection. This is eliminated by ~~completely evacuating the propellant collection system and~~ sweeping out any connecting lines to the Tedlar bag with product before starting sample collection. This procedure will eliminate or reduce nitrogen contamination to less than 0.1% by weight of the sample and the analysis of the propellant gas will be unaffected.

3 APPARATUS AND MATERIALS

3.1 Propellant Collection System [1]: See Figure 1 *(metal cans) and Figure 3 (glass containers)*. ~~The system was built from 1/4" stainless steel and Teflon tubing. The vacuum pump is of bellows diaphragm design~~.

3.2 Tedlar Bags, ~~1 liter,~~ equipped with slip valve and septum

3.3 Density Measurement

3.3.1 250 mL gas dilution bulb, or

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[1] ~~The metal piercing adapter is available from Mid-West Screw Products, Inc., 3523 North Kenton Ave., Chicago, IL 60641. Interim Part Number: 8013A-3/4 Longer SS. The gasket is available from Alltech Associate 2051 Waukegan road, Deerfield, IL 60015, part number 80-16. The glass aerosol adapter is available from Modern Machine Ship, Inc. P.O. Box 826, 123 N. Hazel Street, Danville, IL 61832.~~

3.3.2 Density/Specific gravity meter meeting the following minimum specifications:

~~**3.3.2(a) Measurement Method: Natural Oscillation Type**~~

3.3.2~~**(b)**~~ ***.1*** ***Measurement*** Range: 0 – 3 ***+/- 0.00001*** g/cm^3

3.3.2~~**(c)**~~ ***.2*** Measurement Temperature Range: 4°C ~ 70°C.

~~**3.3.2(d) Temperature Accuracy: +/- 0.02°C (10°C ~ 30°C) and +/- 0.05°C (4°C ~70°C).**~~

~~**3.3.2(e) Temperature Control Accuracy: +/- 0.01°C.**~~

~~**3.3.2(f) Measurement Time: 1- 4 minutes.**~~

3.4 Gas tight syringe, 100 µl

3.5 Balance, capable of accurately weighing to 0.1 mg

3.6 ~~**Can Piercing**~~ ***Sample Venting*** Platform. See Figure 2 (metal cans)[1] and Figure ~~**3**~~ ***4*** (glass containers)[2].

3.7 Platform Shaker, equivalent to Thermolyne M49125

3.8 Cork Rings, 80 x 32 mm

4 PROCEDURE

4.1 Propellant Collection for Metal Aerosol Containers

4.1.1 ~~**Turn on vacuum pump, c**~~***C***lose valves ~~**and evacuate the system**~~ ***on Propellant Collection System*** (see Figure 1).

4.1.2 Remove the valve actuator on the aerosol can and weigh can to the nearest 0.01 g. ~~**Invert the can into cork holding ring on the piercing apparatus, center and snug against the gasket. (Figure 2)**~~

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[1] ***The metal piercing adaptor is available from Mid-West Screw Products, Inc., 3523 North Kenton Ave., Chicago, IL 60641. Interim Part Number: 8013A-3/4 45TAPER REV. The gasket is available from Alltech Associate 2051 Waukegan road, Deerfield, IL 60015, part number 80-16.***

[2] ***The glass aerosol tapered adaptor is available from Armstrong Technologies, Inc. 12780 Earhart Ave., Auburn, CA 95602.***

4.1.3 ~~Connect Tedlar bag to output 2, evacuate bag and seal. Connect 250 mL glass dilution bulb to output 1, evacuate bulb and seal~~. *Place the can in an inverted position onto the Sample Venting Platform, stabilized by cork rings.*

4.1.4 Slowly raise the hydraulic jack until the can is pierced. ~~Record~~ *Note* the pressure of the can.

4.1.5 Vent the can until ~~the pressure is at about 25 psi~~ *propellant is seen flowing from output 1.* Collect the propellant in the Tedlar bag*, from output 1. Density is determined from this same Tedlar bag.*

4.1.6 After the propellant is collected, close and remove the Tedlar bag and vent the remainder of the propellant.

~~4.1.7 Weigh the evacuated 250 mL bulb to the nearest 0.1 mg. Use gloves while handling the bulb. Connect the bulb to the Tedlar bag and open to fill the bulb. Close the valves and re-weigh the dilution bulb, record the weight gain and calculate the propellant density in gm/l.~~

~~4.1.8~~ *4.1.7* After the flow ceases from the can, it is removed from the assembly and allowed to vent overnight~~. The can may be placed~~ on a platform shaker, to vent the remainder of the propellant.

~~4.1.9~~ *4.1.8* Reweigh can to the nearest 0.01 gm and record weight loss (total gms propellant). The can may now be opened for analysis of the ~~liquid product~~ *non-propellant portion of the sample*.

4.2 Propellant Collection for Glass Aerosol Containers

~~4.2.1 Turn on vacuum pump, close valves and evacuate the system (see Figure 1).~~

~~4.2.2 Connect Tedlar bag to output 2, evacuate bag and seal. Connect 250 mL glass dilution bulb to output 1, evacuate bulb and seal.~~

~~4.2.3 The gauge assembly is prepressurized in order to minimize product expulsion and system contamination.~~

~~4.2.4~~ *4.2.1* Remove actuator from valve of the aerosol glass container~~,~~ and weigh container to the nearest 0.01 gm.

~~4.2.5~~ *4.2.2* With container in an inverted position place the valve onto the tapered adaptor, *stabilized by cork rings* . ~~Bring the top plate down to the flat of the container and tighten the nuts. A cork ring may be required to stabilize the container~~

4.2.3 ***Pressurize the air cylinder to actuate the sample container valve onto the tapered adaptor. Note the pressure of the sample container***.

~~4.2.6~~ *4.2.4* ~~**Record pressure of container and vent until the pressure is approximately one-half of recorded pressure**~~ ***Open the sample valve. When propellant is seen flowing from the sampling tubing, c***~~**C**~~ollect propellant sample into the Tedlar bag. ***Density is determined from this same Tedlar bag.***

~~4.2.7~~ *4.2.5* After the propellant is collected, close and remove the Tedlar bag and vent the remainder of the propellant.

~~**4.2.8 Weigh the evacuated 250 mL bulb to the nearest 0.1 mg. Use gloves while handling the bulb. Connect the bulb to the Tedlar bag and open to fill the bulb. Close the valves and re-weigh the dilution bulb, record the weight gain and calculate the propellant density in gm/l.**~~

~~4.2.9~~ *4.2.6* Continue to vent container on the platform assembly ~~**overnight**~~ ***until no pressure registers on the sample gauge and there in no visable propellant flowing from the sampling tube***.

~~4.2.10~~*4.2.7*Remove container from platform ~~**and loosen valve assembly, do not remove valve assembly at this time**~~.

4.2.8 ***Loosen and remove the container valve assembly.***

~~4.2.11~~*4.2.9* Place container on a platform shaker to vent the remainder of the propellant.

~~4.2.12~~*4.2.10* Reweigh container and valve assembly to the nearest 0.01 gm and record weight loss (total gms propellant). The ~~**container may now be opened for analysis of the liquid product**~~ ***non-propellant portion of the sample is ready to be analyzed***.

FIGURE 1

PROPELLANT COLLECTION SYSTEM METAL AEROSOL CONTAINER

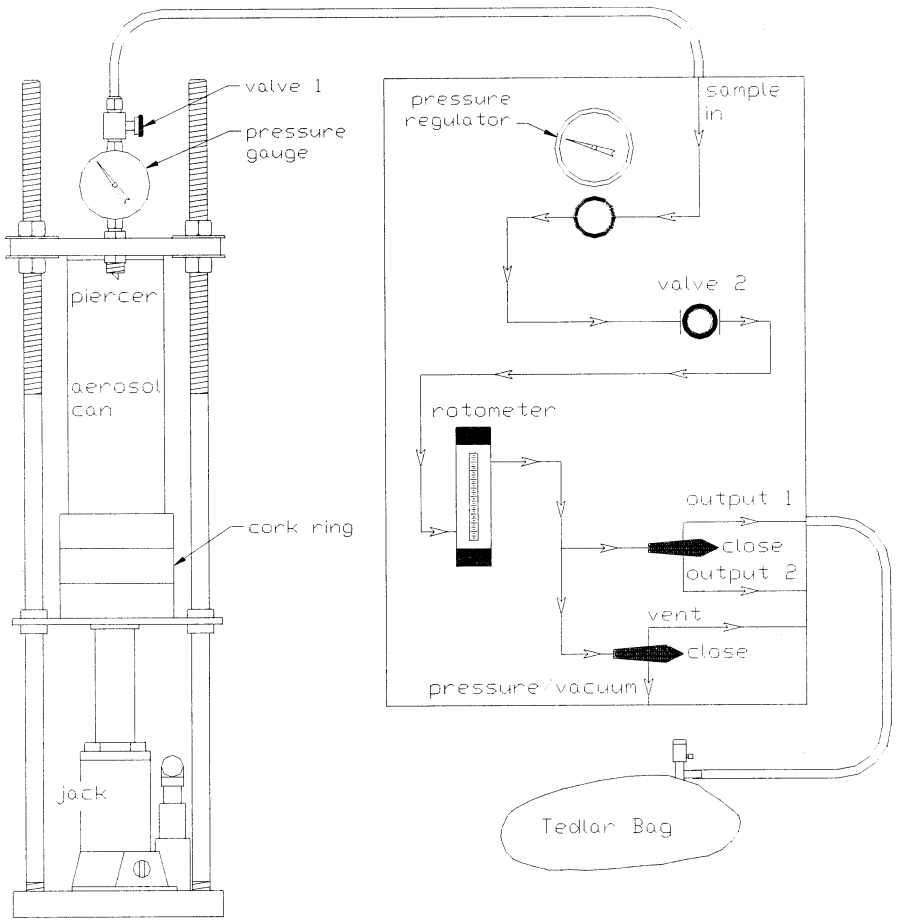


FIGURE 2

SAMPLE VENTING PLATFORM METAL AEROSOL CONTAINER

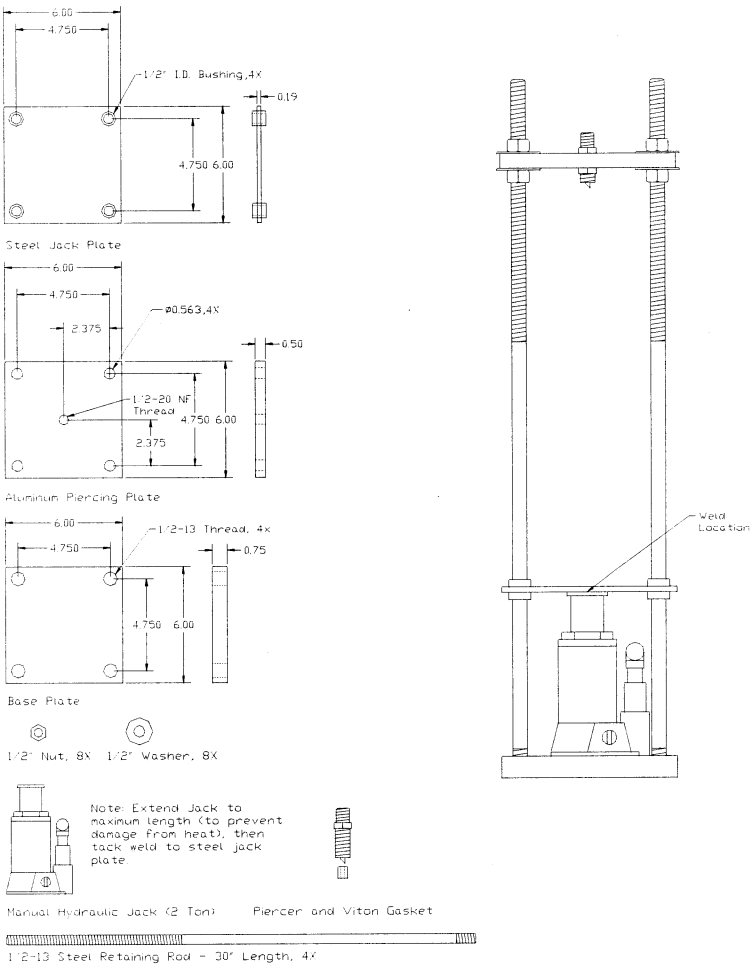


FIGURE 3

PROPELLANT COLLECTION SYSTEM
GLASS AEROSOL CONTAINER

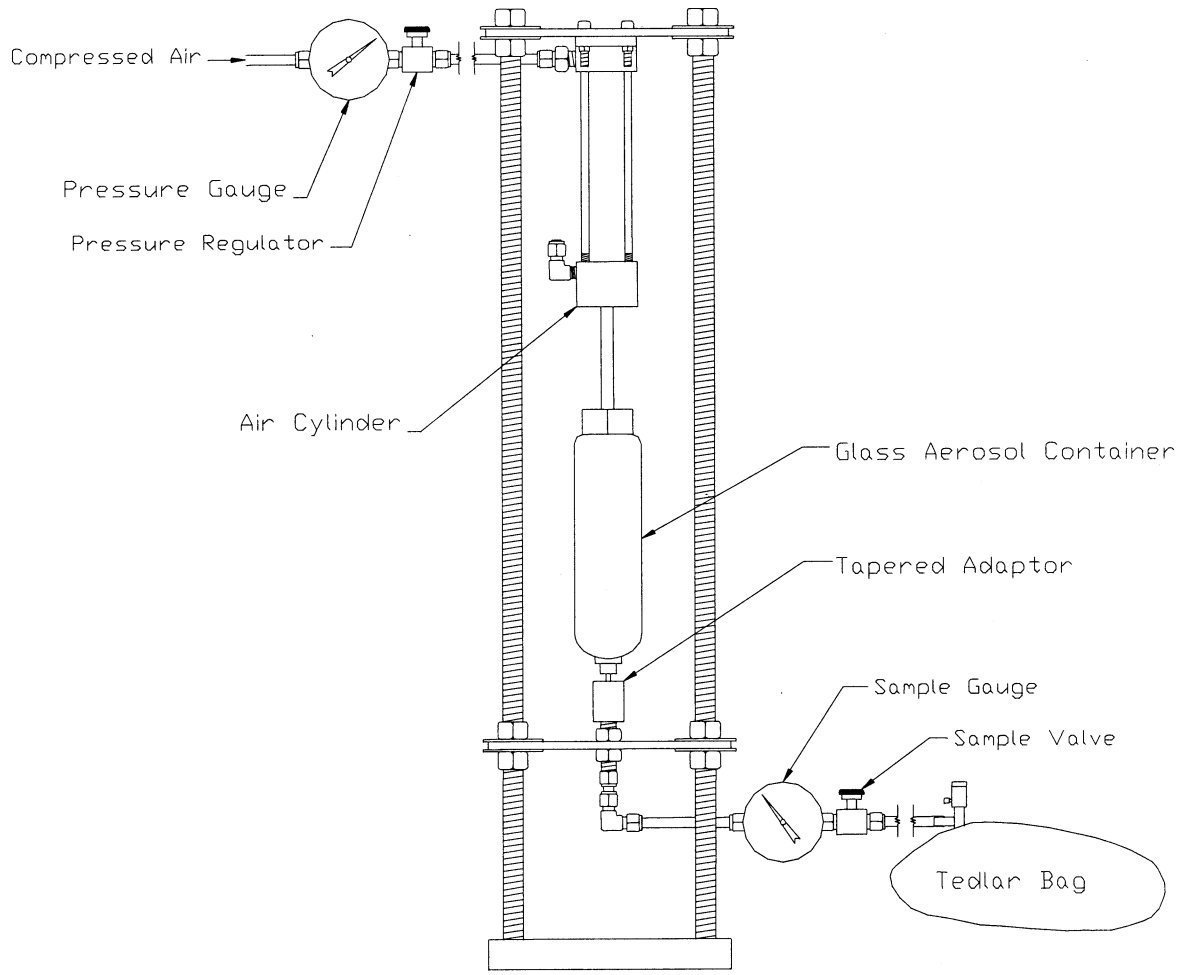
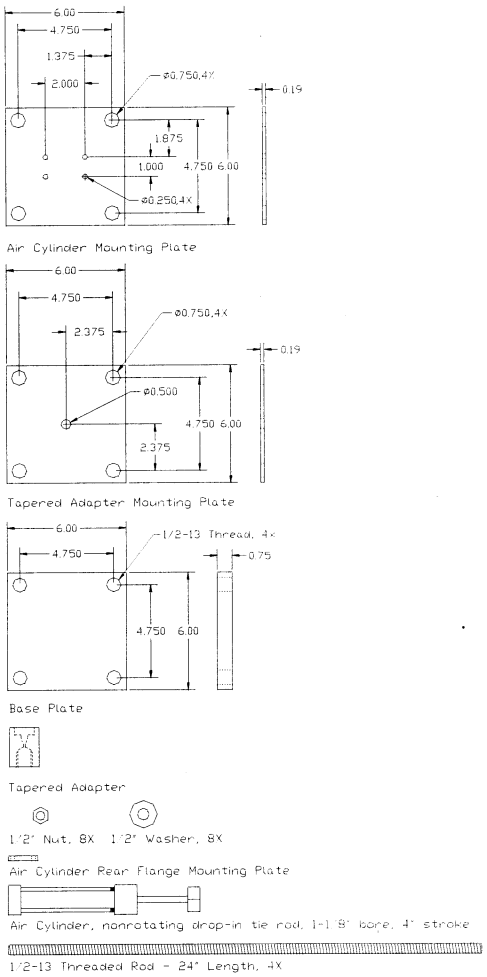


FIGURE 4

SAMPLE VENTING PLATFORM
GLASS AEROSOL CONTAINER



Method 310 - Appendix B

MODIFICATIONS to ASTM D-2879-97 ~~(April 10, 1997)~~

This procedure modifies ASTM D-2879-97 ~~(April 10, 1997)~~ as follows:

1. Modifications to the isoteniscope apparatus include:

    a. capacitance manometers and digital readout
    b. manifold system made of stainless steel and modified in design
    c. Ultra-torr fittings and Ultra-torr flex-lines
    d. ballast on the vacuum side of the isoteniscope manifold as depicted in ASTM D 2879-97 schematics, has been removed.
    e. stainless steel liquid nitrogen trap (Cold Trap)
    f. stainless steel high vacuum valves
    g. recirculating cooling system (required for extremely low pressure work only)
    h. diffusion pump (required for extremely low pressure work only)
    i. hot ion cathode vacuum gauges (required for extremely low pressure work only)

2. A purge and degassing procedure consisting of lower pressures and a liquid nitrogen bath replaces the step of lightly boiling the sample as outlined in ASTM D 2879-97.

3. Purge and Degassing Cycle

    a. With the U-tube connected, the system is evacuated to approximately 1.0 mm Hg. This readily removes most of the higher volatility gases from the sample.

    b. The stainless steel, liquid nitrogen cold trap is filled. The manifold is now brought to approximately 300 mm Hg with the purified nitrogen, regulated through the needle valve.

    c. The isoteniscope tube is carefully placed into a Dewar of liquid nitrogen. The ½ atmosphere pressure of nitrogen prevents the sample from splashing while being frozen. After the sample freezes, the system is evacuated to 0.05 mm Hg.

    d. The U-tube is removed from the Dewar, secured and allowed to warm to room temperature. The U-tube bulb head should be angled so the dissolved gases will be readily evacuated as the frozen sample starts to melt. When gases build up, it may be necessary to tilt the U-tube to release the gases.

    e. Repeat the freeze and degas process once, reducing pressure each time to less than 0.05 mm Hg. After the sample has returned to room temperature, close valve #3. There should be minimal dissolved gases left once the frozen sample starts to melt. Tilt the tube to release any gas pockets (if necessary). Do not push nitrogen into the evacuated

space between the sample in the arm and the sample in the reservoir. At this point, if the sample is properly degassed, a "natural break" should form in the sample. This creates a vapor space as the liquid level in the bulb leg of the manometer falls to a quasi-equilibrium position, usually with the fluid level higher in the long manometer leg. If there is no pendulum effect, and the liquid level in the long leg of the manometer is significantly higher than the level in the short leg (> 2 mm), degassing is probably incomplete, and the degassing procedure should be repeated.

4. Data Evaluation

The regression based on the plot of Log P vs. 1/T as outlined in ASTM D 2879-97 has been removed and replaced with a nonlinear regression to generate the coefficients for an Antoine equation. The data analysis procedure assumes that the measured pressure is the sum of the compound's vapor pressure and a residual fixed gas pressure. The vapor pressure's dependence on absolute temperature is represented by an Antoine expression, and the fixed gas as pressure is directly proportional to absolute temperature as outlined in ASTM 2879. This leads to the model equations:

$$P_{model} = P_{vapor} + P_{fixed\ gas}$$

$$P_{model} = B0 * 10^{(B1/(T+B2))} + B3 * T$$

where T is the absolute temperature (K) and B0, B1, B2 and B3 are coefficients to be determined via a nonlinear regression which minimizes the sum of squares $\sum (P_{meas} - P_{model})^2$ for all experimental data points. The vapor pressure at 20° C is then calculated as:

$$P_{vapor}\ (293.15\ K) = B0 * 10^{(B1/(293.15+B2))}$$

With a set of pressure vs. temperature measurements, the nonlinear regression can be performed using a statistical software packages. The following constraints are imposed to obtain meaningful Antoine equation coefficients for low vapor pressure samples:

a. Pressures shall be measured at temperatures ranging from room temperature to about 180° C. Narrower ranges will not provide sufficient information to determine the

Antoine curvature, i.e., B2 coefficient. Wider ranges can lead to experimental difficulties maintaining the vapor space in the isoteniscope. A minimum of 12 points is necessary to provide ample degrees of freedom for the calculations.

b. Initial pressures at room temperature shall be less than 1 mm Hg. Higher values are indicative of significant levels of dissolved fixed gases. These will vaporize during the course of the experiment as temperature is increased and invalidate the model's assumption for the fixed gas contribution.

c. $-235 \leq B\,2 \leq 0$. Positive values of B2 imply that the heat of vaporization of the substance increases with increasing temperature. Thermodynamic data for many compounds suggests this is unrealistic. Large negative values can lead to unrealistically low vapor pressure values coupled with excessive fixed gas contributions. The -235(K) bound is chosen to be consistent with literature values of B2 for many pure compounds. For hydrocarbons in the LVP-VOC range, $B2 \geq -100$ provides reasonable agreement between measured and literature vapor pressures.

d. The fixed gas coefficient, B3, should normally be ≥ 0.

Figure 1

ISOTENISCOPE VAPOR PRESSURE MEASUREMENT APPARATUS